PROPERTY ENHANCEMENT OF WOOD–RUBBER COMPOSITES BY MICROWAVE TREATMENT OF RUBBER PARTICLES

*Min Xu**†

Professor
E-mail: donglinxumin@163.com

Jian Li†

Professor
Northeast Forestry University
Harbin 150040, PR China
E-mail: nefulijian@163.com

Sheldon Q. Shi†

Associate Professor
E-mail: Sheldon.Shi@unt.edu

Liping Cai

Researcher
Mechanical and Energy Engineering Department
University of North Texas
Denton, TX
E-mail: Liping.Cai@unt.edu

(Received March 2014)

Abstract. In this study, a microwave oven with a frequency of 2450 MHz was used for the surface modification of rubber particles. The samples were treated with five different output powers (160, 320, 480, 640, and 800 W) for six exposure times (1, 2, 3, 4, 5, and 6 min). The influence of the microwave treatment on rubber characteristics was analyzed by Fourier transform infrared spectroscopy. The wood–rubber composites were fabricated using 70% poplar particles and 30% rubber particles. Four regression equations, ie radiation time and power as functions of modulus of rupture, modulus of elasticity, internal bond, and thickness swelling, were developed and a nonlinear programing model was derived to obtain the optimum panel properties. The results from contact angle measurements and microscopic analysis indicated that the surface characteristics were changed after the microwave treatment, improving the mechanical properties of the wood–rubber composites.

Keywords: Microwave treatment, rubber superficial characteristics, panel properties, nonlinear programing.

INTRODUCTION

A large number of waste tires is discarded every year, which represents a crucial environmental problem. Driven by green solutions for the life cycle of consumer and industry products using discarded tires, interest has arisen in the development of wood–rubber composites during the past decade (Zhao et al 2008, 2010; Ayrilmis et al 2009a, 2009b; Li et al 2009; Prompunjai and Sridach 2010; Xu and Li 2012). These studies showed that dimensional stability, water resistance, energy absorption, and sound insulation of wood–rubber were improved compared with neat wood composites.

An environmentally friendly composite combining sawdust, cassava starch, and natural latex rubber was developed by Prompunjai and Sridach (2010). It was demonstrated that brittle failure decreased and flexural strength increased

* Corresponding author
† SWST member

by incorporating rubber into the composite formulation. The influence of panel density, pressing time, and temperature on internal bond (IB), modulus of rupture (MOR), and modulus of elasticity (MOE) of wood–rubber composites was investigated by Zhao et al (2008). Optimal panel manufacturing conditions were pressing temperature of 170°C for 300 s and panel density of 1000 kg/m^3. Because of the addition of rubber, improved sound insulation of the composite was reported in their later study (Zhao et al 2010). Waste tire rubber particles were used in the manufacture of particleboard (Ayrilmis et al 2009a). Although MOR values were decreased by 12-58% because of the rubber, the dimensional stabilities, such as resistance to thickness swelling (TS), were improved by 9-53%. Ayrilmis et al (2009b) also incorporated the rubber particles into the oriented strandboard (OSB) and found that the IB values of the OSB panels decreased by 16-50%, whereas the water resistance considerably improved. In an attempt to obtain the relationship between the production conditions and penal properties, four regression equations (rubber content, pressing temperature, resin content, and target panel density as functions of MOR, MOE, IB, and TS) were developed by Xu and Li (2012). Furthermore, using a nonlinear programing model, the most desirable panel properties could be achieved under some production constraints.

Plasma is a relatively new technology used to improve some rubber surface properties. The surface characteristics of the ethylene propylene diene monomer (EPDM) rubber were modified using microwave-excited plasma (2.45 GHz, 1 kW) by Keshri et al (2009) and Oliveira et al (2010). With examinations of contact angles and atomic force microscopy, it was concluded that contact angles (with deionized water) were significantly decreased by the treatments, indicating improvement in rubber surface energy.

To improve the adhesion properties of EPDM rubber for thermal protection of rocket chambers, a radiofrequency plasma treatment was used by Moraes et al (2007). The surface properties were examined using contact angle measurements and X-ray photoelectron spectroscopy. A significant decrease in contact angle was found after treatment, indicating an increase in surface energy. Compared with untreated rubber, an improvement of about 30% in adhesion strength was obtained for the treated EPDM–polyurethane liner interface and 110% for the EPDM–epoxy adhesive interface.

Kim et al (2010) investigated the adhesion force between a chloride-isobutene-isoprene rubber (CIIR) and stainless steel ball and found that high-density microwave plasma treatment using oxygen and argon gases would decrease the adhesion force of the rubber. The contact area also decreased with treatment time, and a dramatic change was observed after a 5-min treatment of CIIR. The field emission scanning electron microscope image also showed that the subsurface of the CIIR pattern changed with various plasma treatments. These results implied a change in the morphology of the CIIR surface by plasma treatment, which was one reason for the decrease in adhesion forces.

Microwave treatment heats materials with some polarity rapidly and uniformly because of the dipole rotation of molecules induced by microwaves (Scuracchio et al 2007). Carbon black, a common component used in tire rubber, is characterized by its polarity. It makes the microwave heating possible to treat tire rubber efficiently. The use of microwave energy allows heat propagation inside the material, improving the efficiency of heat transfer at decreased processing times with energy savings. The dielectric properties of some rubber materials under microwave frequencies of 26 and 9.6 GHz were examined by Gunasekaran et al (2008). It was found that rubber materials could be heated by microwave radiation because their dielectric constants varied from 1.15 to 8.63. Dielectric behavior of natural rubber composites in microwave fields at a frequency of 2-4 GHz was investigated by John et al (2007). By adding polyaniline powder, a conductive rubber material was obtained.

Microwave treatment of rubber tires promotes some changes in the rubber structure and composition. With a frequency ranging from 300 MHz to 300 GHz, microwave electromagnetic radiation can be absorbed by material through molecular interaction with the electromagnetic field and can be converted to heat (Hirayama and Saron 2012). The cores of rubber particles can obtain energy through radiation, not rely on diffusion of heat from surfaces. Using microwave treatment, Hirayama and Saron (2012) devulcanized rubber and then modified it by chemical methods. After microwave devulcanization, the rubber with a lower content of carbon black showed an increase in crosslink density.

To improve adhesion characteristics, ground tire rubber was treated by microwaves for different exposure times (from 1 to 5 min) at a constant power level (Scuracchio et al 2007). It was found that the microwave treatment changed the thermal behavior and decreased the glass transition temperature, probably because of the modification in the chemical structure of the rubber. Partial devulcanization of a poly (ethylene-propylene-diene) rubber filled with carbon black was treated by a microwave-thermal method at temperatures greater than 300°C (Bani et al 2011). It was found that microwave treatment was a very fast and simple technique and was able to lower the degree of crosslinking. As a result, good interface adhesion was achieved.

Bromobutyl rubber was devulcanized using microwave treatments at a frequency of 2.45 GHz by Landini et al (2007). Rubber samples, each weighing 250 g, were irradiated at powers of 1000, 2000, and 3000 W for 9-25 min. After the hardness measurements and ash tests, the best operation conditions were obtained at 2000 W for 13 min.

This study was aimed at investigating the effect of microwave treatment of rubber particles on surface characteristics and properties of wood–rubber composites.

MATERIALS AND METHODS

Rubber particles sourced from disposed tires, with an average size of 600 μm (from 80 to 800 μm), were used in this study. According to Scuracchio et al (2007), the major components of most tire rubber are natural rubber, styrene-buta-diene copolymer, polybutadiene, and carbon black. The rubber powders were treated in a microwave oven (G80F23CSL-A9) that had a frequency of 2450 MHz and a variable output power from 160 to 800 W. Thus, the variables adopted here were the output powers (160, 320, 480, 640, and 800 W) and exposure times (1, 2, 3, 4, 5, and 6 min). Although the exact power density applied was difficult to determine, the heat generated in the rubber particles can be increased with an increase in output power and radiation time because a constant amount (30 g) of rubber particles was used for each treatment.

Poplar (*Populus* spp.) flakes (with a length ranging from 3 to 20 mm, a width ranging from 0.8 to 2.2 mm, and a thickness ranging from 0.2 to 0.6 mm) and rubber particles were dried to moisture contents of 4 and 3%, respectively. Polymeric methylene diphenyl diisocyanate (pMDI) resin was used as an adhesive for the composite fabrication. A drum-type laboratory blender was used to mix wood particles and rubber powder. After the pMDI resin was sprayed into the wood and rubber mixture, the furnish was manually formed into a mat of 340 × 320 mm. The mat was prepressed at 3 MPa for about 1 min and then hot-pressed to a target thickness of 10 mm. The panels were made with a rubber content of 30% of the wood–resin mixture, hot-pressing temperature of 160°C, resin content of 3%, and target panel density of 800 kg/m^3. Four replicate panels were made for each microwave treatment condition. There were 12 combinations of radiation time and power plus one control (without any treatment), resulting in a total of 52 panels (Table 1). The panel properties (MOR, MOE, IB, and TS) were determined according to Chinese Standard (2003). Prior to the measurements, all specimens were conditioned at 65% RH and 20°C for 4 wk. For each panel type, 12 specimens (50 × 250 mm) were used for the bending test and six specimens (50 × 50 mm) were used for IB and TS tests, respectively.

Table 1. Panel properties under different treatment times and powers.

No.	Radiation time (s)	Radiation power (W)	MOR[a] (MPa)	MOE[a] (MPa)	IB[a] (MPa)	TS[a] (%)
1	0	0	19.72	2068.45	0.62	4.8
2	60	480	23.85	2452.42	0.81	4.88
3	120	160	23.02	2310.31	0.79	4.89
4	120	320	23.31	2310.46	0.85	4.92
5	120	480	23.02	2426.08	0.84	4.88
6	120	800	21.81	2347.04	0.78	4.94
7	120	640	24.15	2438.59	0.96	4.89
8	180	480	23.12	2412.05	1.13	4.92
9	180	640	25.05	2639.41	0.95	4.93
10	240	320	23.54	2518.72	1.09	4.92
11	240	480	22.74	2392.13	0.99	4.89
12	300	160	22.82	2327.54	0.87	4.91
13	360	480	22.28	2317.22	0.8	4.94

[a] MOR, modulus of rupture; MOE, modulus of elasticity; IB, internal bond; TS, thickness swell.

Relationships between the microwave treatment conditions (radiation time and power strength) and the properties of the wood–rubber composites were analyzed using multiple variable nonlinear regression. Operations research was used to derive values for system variables that will optimize performance. To achieve the most desirable panel properties, an optimal combination of radiation time and output power was designed.

Furthermore, Fourier transform infrared (FTIR) spectroscopy was used to analyze the differences in chemical structure of the rubber particles before and after microwave treatment. The contact angles of the panel surfaces were examined using a JC200c Goniometer (Zhongchen Numeric Technology Equipment Ltd., Shanghai, China). The measurements were completed right after a drop of liquid was placed on the specimen surface. Two probe liquids were used: deionized water and di-iodine methane. The values presented here are averages of six measurements at different places on the specimen surfaces.

With an FEI (Hillsboro, OR) QUANTA200 scanning electron microscope (SEM), the ultrastructures of the wood–rubber composites before and after microwave radiation treatment of the rubber particles were examined. Twenty- × 20- × 20-mm specimens were cut from the section on the broken positions during tension tests. With a microtome, 20-μm-thick slices with a smooth surface were obtained. All the dried slices were placed on sample holders using double-sided adhesive tape.

RESULTS AND DISCUSSION

Effect of Microwave Treatment Conditions on Panel Properties

Table 1 presents the properties of the panels prepared using rubber particles that were microwave-treated with different radiation times (from 60 to 360 s) and output powers (from 160 to 800 W). The properties of panels with untreated rubber particles are given in the first row in Table 1. Compared with the properties of the panels made with untreated rubber, MOR, MOE, and IB were significantly increased ($p < 0.05$) because of the microwave pretreatment. Rubber cannot be easily adhered with other materials because of its crosslinked nature (Bani et al 2011). Microwave treatments can lower the degree of crosslinking and enhance interface adhesion of rubber with wood and resin. As a result, improved panel properties, such as MOR, MOE, and IB, were obtained.

As shown in Table 1, TS of the wood–rubber composites was slightly increased by 0.14% (from 4.8 to 4.98%) because of the microwave treatment, although the statistical analysis from analysis of variance did not show significance at $p < 0.05$. Microwave treatment can break the crosslinks, mainly in polysulfidic bonds

(Hirayama and Saron 2012), which could increase the rubber hygroscopicity.

Figures 1 and 2 show that MOR and MOE were polynomial functions of radiation time and output power. Figure 3 illustrates that IB was also a polynomial function of radiation time. Although an increase in radiation intensity or time could help increase oxygen content, the C-O bonds resulting from oxygen activation might be broken if radiation intensity was too high or treatment time was too long.

As a linear function, the relationship of radiation time with TS is shown in Fig 3. The relationship between the output power and IB was a polynomial curve, whereas TS was linearly increased with an increase in output power.

During initial microwave pretreatment, as radiation time or output power increased, the temperature in rubber particles increased rapidly. Those high temperatures during microwave treatment increased the amount of hydroxyl groups on rubber surfaces, which enhanced the hydrophilicity of the rubber in the composites. One negative result of microwave treatment is that more water or moisture can be absorbed by rubber in the composite and the TS of the panels can correspondingly increase.

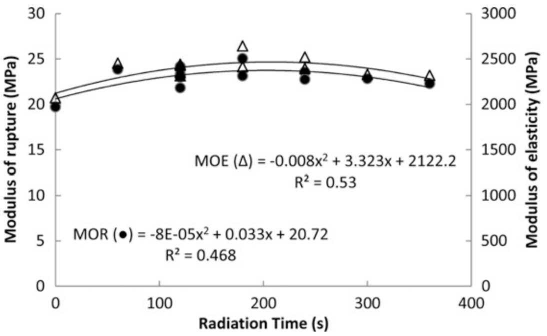

Figure 1. Modulus of rupture (MOR) and modulus of elasticity (MOE) as functions of radiation time.

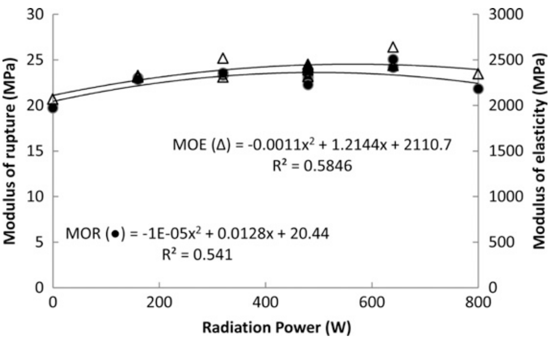

Figure 2. Modulus of rupture (MOR) and modulus of elasticity (MOE) as functions of radiation power.

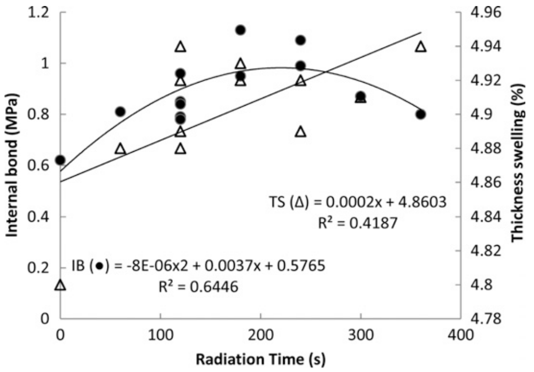

Figure 3. Internal bond (IB) and thickness swell (TS) as functions of radiation time.

Nonlinear Regression

Based on the experimental data, four regression equations (radiation time and radiation power as functions of MOR, MOE, IB, and TS) were obtained as follows:

$$\begin{aligned}\mathrm{MOR} = {} & 19.813 + 0.017\mathrm{x}_1 - 3.564\mathrm{E} \\ & - 05(\mathrm{x}_1)^2 + 0.012\mathrm{x}_2 - 1.059\mathrm{E} \\ & - 05(\mathrm{x}_2)^2 - 1.244\mathrm{E} - 05\mathrm{x}_1\mathrm{x}_2 \end{aligned} \quad (1)$$

$R^2 = 0.697$

$$\begin{aligned}\mathrm{MOE} = {} & 2054.455 + 1.865\mathrm{x}_1 \\ & - .0045(\mathrm{x}_1)^2 + 0.858\mathrm{x}_2 \\ & - .0007(\mathrm{x}_2)^2 \end{aligned} \quad (2)$$

$R^2 = 0.695$

$$\begin{aligned}\mathrm{IB} = {} & 0.571 + 0.003\mathrm{x}_1 - 8.58\mathrm{E} - 06(\mathrm{x}_1)^2 \\ & + 0.00036\mathrm{x}_2 - 6.68\mathrm{E} - 07(\mathrm{x}_2)^2 \\ & + 1.265\mathrm{E} - 06\mathrm{x}_1\mathrm{x}_2 \end{aligned} \quad (3)$$

$R^2 = 0.717$

$$TS = 4.8268 + 0.00022x_1 + 8.823E - 05x_2 \quad (4)$$

$$R^2 = 0.695$$

where x_1 is the radiation time (s); x_2 is the radiation power (W); and R is the correlation coefficient of each regression.

With these four equations, MOR, MOE, IB, and TS of a panel can be predicted based on microwave pretreatment conditions, ie radiation time and power level.

Optimization

With the microwave treatment at a frequency of 2.45 GHz, an optimal operation condition for devulcanizing bromobutyl rubber was 2000 W for 13 min (Landini et al 2007). Since polynomial relationships existed between the independent variables (microwave treatment time and output power) and the dependent variables (MOR, MOE, and IB), there was a need to explore the optimal microwave treatment conditions for the rubber particles. With nonlinear programming, an optimization model was developed as follows. In cases in which the maximum MOR is desired for the panels and the standards of furniture particleboards (Chinese Standard 2003) require minimum MOR, MOE, and IB of 14, 1800, and 0.4 MPa, respectively, and maximum TS of 8%, nonlinear programming can be formed as follows:

Maximum:

$$F(X) = 19.813 + 0.017x_1 - 3.564E - 05(x_1)^2 + 0.012x_2 - 1.059E - 05(x_2)^2 - 1.244E - 05x_1x_2$$

subject to

$$MOE = 2054.455 + 1.865x_1 - .0045(x_1)^2 + 0.858x_2 - .007(x_2)^2 \geq 1800$$

$$IB = 0.571 + 0.003x_1 - 8.58E - 06(x_1)^2 + 0.0004x_2 - 6.68E - 07(x_2)^2 + 1.265E - 06x_1x_2 \geq 0.4$$

$$TS = 4.8268 + 0.00022x_1 + 8.823E - 05x_2 \leq 0.08$$

where x_1 is the radiation time, s, and x_2 is the output power, W.

Because the radiation time was from 60 to 360 s and the output power was from 160 to 800 W, the experimental condition constraints were as follows: $60 \leq x_1 \leq 360$; $160 \leq x_2 \leq 800$.

The optimal solution for the problem is $(x_1, x_2) = (160, 460)$ with a maximum $F(X) = 23.80$. The results indicate that a maximum MOR of 23.8 MPa of the panels can be obtained when the radiation time of 160 s and output power of 460 W are used. This makes MOE, IB, and TS for the panel equal to 2460.8 MPa, 0.98 MPa, and 4.90%, respectively, which meet the requirements of furniture particleboards according to the standards (Chinese Standard 2003).

Fourier Transform Infrared Spectroscopy

FTIR spectroscopy is a useful tool for examining chemical changes in organic compounds. A comparison of the spectra between the rubber particles before and after microwave treatment was carried out to explore the molecular changes that occurred. Figure 4 shows that the absorption bands located around 3300 cm^{-1} were enlarged after microwave treatment at an output power of 480 W for 180 s. Those bands were typically attributed to stretching of C-H bonds. Enlargement of these bands could be associated with the

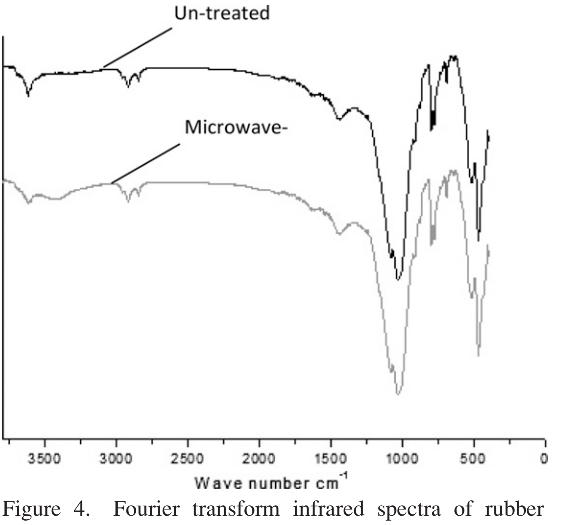

Figure 4. Fourier transform infrared spectra of rubber before and after microwave treatment under an output power of 480 W for 180 s.

interpolation of absorption bands of chemical groups such as hydroxyl and amides (Hirayama and Saron 2012). The increased activation groups and polarization on the rubber surfaces probably benefited the bonding property among the rubber particles, wood chips, and MDI resin. This could in turn lead to improving the panel properties, such as IB and MOR.

Contact Angle Analysis

Contact angle development as a function of rubber microwave treatment time is given in Table 2. When the radiation power remained a constant value of 480 W, the minimum contact angle value of 116.5° was obtained at the radiation time of 180 s, indicating that the rubber surface reached the maximum wettability for such treatment condition. It may not produce enough surface energy to maximize its wettability if the treatment time was shorter than this value. Conversely, it appeared that more oxygen groups were grafted on the rubber surface if the treatment time was longer than this value. The long treatment time could also increase the crosslinks on the rubber surface, which decreased the number of available sites for polar groups to incorporate (Oliveira et al 2010).

Contact angle changes as functions of output power are illustrated in Table 3. When a constant radiation time of 120 s was used, a minimum contact angle of 121.1° was observed under a power of 480 W. If a higher radiation power than this value was applied to the rubber surface, the intensive radiation could break the C-O bonds, resulting in a decrease in wettability on the rubber surfaces. Smaller contact angles led to greater adhesion strength. In this regard, Moraes et al (2007) indicated that, through radiation treatment, adhesion strength for the treated EPDM–polyurethane liner interface and for the EPDM–epoxy adhesive interface could be improved by 30 and 110%, respectively.

Table 2. Contact angle changes with radiation time.

Radiation power (W)	480					
Radiation time (s)	60	120	180	240	300	360
Contact angle (°)	126.3	121.1	116.5	118.1	121.6	125.2

Table 3. Contact angle changes with radiation power.

Radiation time (s)	120				
Radiation power (W)	160	320	480	640	800
Contact angle (°)	127.4	125.2	121.1	121.4	125.5

Microscopic Analysis

SEM images of tensile-fracture surfaces of composites made by untreated and microwave-treated rubber particles are shown in Figs 5 and 6. Figure 5 illustrates that for wood and untreated rubber composites, the two primary components were not well bonded. Because of the loose structure, obvious fractures and gaps were easily observed, indicating poor interfacial bonding between rubber and wood particles (Fig 5). With the microwave-treated rubber, a microscopic structure with smaller gaps was observed in the panels (Fig 6).

CONCLUSIONS

Microwave treatment of rubber particles significantly increased MOR, MOE, and IB of wood–rubber composites. The improvements

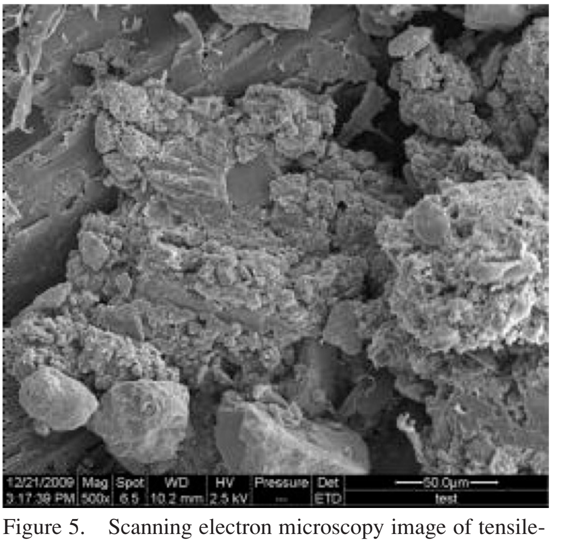

Figure 5. Scanning electron microscopy image of tensile-fracture surfaces of untreated rubber composite.

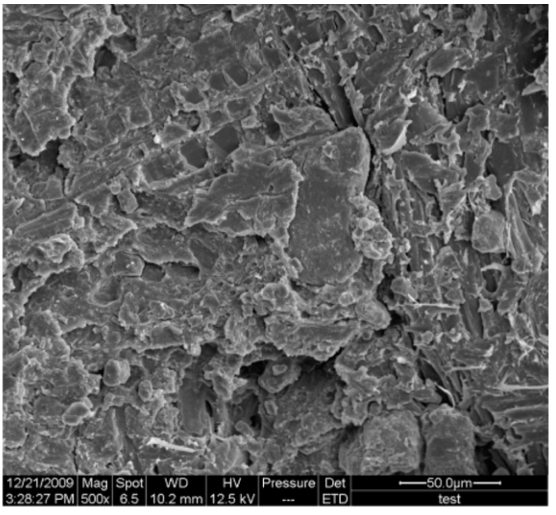

Figure 6. Scanning electron microscopy image of tensile-fracture surfaces of rubber composite after microwave treatment at 480 W for 3 min.

were caused by the increase in interfacial bonding between rubber and wood fibers as shown in the contact angle measurements and microscopic analysis. Four regression equations (Eqs 1-4) were developed. Given the radiation time and power level, the composite properties can be estimated. With the nonlinear programing, the desired MOR, MOE, IB, or TS could be obtained under certain microwave treatment conditions. The optimal microwave treatment condition was output power of 460 W for 160 s to obtain maximum MOR of the wood–rubber panels.

ACKNOWLEDGMENTS

This study was financially supported by the Natural Science Foundation of Heilongjiang Province, China, through grant number ZD201306.

REFERENCES

Ayrilmis N, Buyuksari U, Avci E (2009a) Utilization of waste tire rubber in the manufacturing of particleboard. Mater Manuf Process 24(4):688-692.

Ayrilmis N, Buyuksari U, Avci E (2009b) Utilization of waste tire rubber in manufacture of oriented strandboard. Waste Manag 29(5):2553-2557.

Bani A, Polacco G, Gallone G (2011) Microwave-induced devulcanization for poly (ethylene-propylene–diene) recycling. J Appl Polym Sci 120(11):2904-2911.

Chinese Standard (2003) GB T4897.1-7. Chinese standards for particleboard—Parts 1–7 [in Chinese].

Gunasekaran S, Natarajan RK, Kala A, Jagannathan R (2008) Dielectric studies of some rubber materials at microwave frequencies. Indian J Pure Ap Phy 46(4):733-737.

Hirayama D, Saron C (2012) Chemical modifications in styrene-butadiene rubber after microwave devulcanization. Ind Eng Chem Res 51(8):3975-3980.

John H, Joseph R, Mathew KT (2007) Dielectric behavior of natural rubber composites in microwave fields. J Appl Polym Sci 103(12):2682-2686.

Keshri AK, Bakshi SR, Chen Y, Laha T, Li X, Levy C, Agarwal A (2009) Nanomechanical behavior of plasma sprayed PZT coatings. Surf Eng 25(4):270-275.

Kim JH, Nitta I, Umehara N, Kousaka H, Shimada M, Hasegawa M (2010) Plasma treatment of CIIR rubber with improvement of adhesion and real contact area. Int J Mod Phys B 24(15/16):2688-2693.

Landini L, Araújo SGdA, Lugão B, Wiebeck H (2007) Preliminary analysis to BIIR recovery using the microwave process. Eur Polym J 43(12):2725-2731.

Li X, Levy C, Agarwal A, Datye A, Elaadil L, Keshri AK, Li M (2009) Multifunctional carbon nanotube film composite for structure health monitoring and damping. The Open Construction and Building Technology Journal 3(1):146-152.

Moraes JH, Sobrinho ASdS, Maciel HS, Dutra JCN, Massi M, Mello SAC, Schreiner WH (2007) Surface improvement of EPDM rubber by plasma treatment. J Phys D Appl Phys 40(11):7747-7752.

Oliveira MS, Mello SAC, da Silva Sobrinho AS, Grigorov KG, Massi M, Maciel HS, Dutra JCN (2010) Surface modification of EPDM rubber by microwave excited plasmas. Surf Eng 26(7):519-524.

Prompunjai A, Sridach W (2010) Preparation and some mechanical properties of composite materials made from sawdust, cassava starch and natural rubber latex. World Academy of Science, Engineering and Technology 72(7):930-934.

Scuracchio CH, Waki DA, da Silva MLCP (2007) Thermal analysis of ground tire rubber devulcanized by microwaves. J Therm Anal Calorim 87(3):893-897.

Xu M, Li J (2012) Effect of adding rubber powder to poplar particles on composite properties. Biores Technol 118(1):56-60.

Zhao J, Wang X, Chang J, Zheng K (2008) Optimization of processing variables in wood-rubber composite board manufacturing technology. Biores Technol 99(5):2384-2391.

Zhao J, Wang XM, Chang J, Yao Y, Cui Q (2010) Sound insulation property of wood-waste tire rubber composite. Compos Sci Technol 70(14):2033-2038.